

Highly Selective V-P-O/ γ -Al₂O₃ Catalysts in the Ammoxidation of Toluene to Benzonitrile†

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γ -Al₂O₃-supported vanadium phosphorus oxide catalysts prepared by solid-solid wetting for the first time are highly active and selective for the ammoxidation of toluene to benzonitrile at 400 °C and the ammonia uptake of the catalysts correlates directly with their ammoxidation activity.

Vanadium phosphorous oxide (V-P-O) catalysts are used industrially for the selective oxidation of n-butane to maleic anhydride.^{1,2} Industrial V-P-O catalysts capable of activating alkanes for partial oxidation are typically prepared in alcohol solution and are highly active and selective.^{3,4} Advantages have been claimed for the use of organic solvents and reducing agents in the synthesis of V-P-O catalyst precursors. In particular, the surface areas of the precursors are higher than for precursors prepared in aqueous media.⁵

The application of V-P-O catalysts for the oxidation-ammoxidation of alkyl aromatics to the corresponding aldehydes-nitriles has not been studied much. The preparation of nitriles in good yields *via* ammoxidation of picolines using α -VOPO₄ has been described.⁶

The ammoxidation of toluene to benzonitrile is an industrially important reaction. Benzonitrile is used in the synthesis of benzoguanamine, which is a derivative of melamine and is used in protective coatings and moulding resins. Titania-supported vanadium oxide catalysts are active and selective for the ammoxidation of alkyl aromatic compounds.⁷⁻⁹ In this communication we report for the first time the ammoxidation of toluene with high selectivity (98%) for benzonitrile formation over vanadium phosphorous oxide supported on γ -Al₂O₃ prepared by solid-solid wetting. A direct correlation has been found between the NH₃ chemisorption capacities of the catalysts and toluene conversion to benzonitrile.

V₂O₅ (25 g) was stirred in a mixture of isobutyl alcohol (250 ml) and benzyl alcohol (25 ml) and heated under reflux for 12 h. After cooling to room temp., the requisite amount of 88% orthophosphoric acid was added to give a P:V atomic ratio of 1:1 in the final catalyst. The mixture was heated under reflux for another 12 h, cooled, filtered and dried at 150 °C for 12 h. Since the V-P-O had been prepared in an organic medium, γ -Al₂O₃ [Harshaw, Brunauer-Emmett-Teller (BET) surface area 206 m² g⁻¹] supported V-P-O catalysts of

different loadings were prepared by the solid-solid wetting technique. Appropriate quantities of V-P-O and γ -Al₂O₃ powders were mixed and finely ground in an agate mortar for 20 min, and then calcined at 400 °C for 6 h. The X-ray powder diffraction patterns of the calcined catalysts showed that the V-P-O at all loadings (2–20 wt%) was well dispersed on the γ -Al₂O₃ support. A fixed-bed flow microreactor operating under normal atmospheric pressure was used to determine the activities of the catalysts at 400 °C. About 1 g of the sample (particle size, *ca.* 0.7 mm) was used for activity studies in the ammoxidation of toluene. Toluene, air and ammonia with flow rates of 1 ml h⁻¹, 5.4 l h⁻¹ and 2.8 l h⁻¹, respectively, with a contact time of 0.44 s, were passed over the catalyst bed maintained at 400 °C. The cooled products (–10 °C) contained mainly benzonitrile and unconverted toluene, with small amounts of CO and CO₂, and were analysed by gas chromatography using an OV-17 column and a flame ionization detector. The catalysts were characterized by their BET surface area and ammonia chemisorption at room temp. by procedures which have been described elsewhere.¹⁰

The BET surface area, ammonia uptake, conversion and selectivity to benzonitrile of various catalysts are presented in Table 1. The V-P-O/ γ -Al₂O₃ catalysts are active and highly selective for the ammoxidation of toluene to benzonitrile, the toluene conversion increasing to 64% with as the V-P-O

Table 1 BET surface areas, ammonia uptake and toluene conversion to benzonitrile of for various V-P-O/ γ -Al₂O₃ catalysts

V-P-O loading (wt. %)	BET surface area/m ² g ⁻¹	NH ₃ uptake/ μ mol g ⁻¹	Toluene conversion (%)
2	198	104	4.2
5	149	273	8.5
8	146	395	18.1
12	133	811	32.1
15	115	1192	63.4
20	78	1361	64

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loading increases up to 15 wt%. The selectivity for formation of benzonitrile does not vary with the V-P-O loading, and was 98% for all catalysts studied. It is significant that benzene, the dealkylation product, is not formed. The most commonly held view is that the presence of phosphorus stabilizes the V^{4+} oxidation state (relative to V^{5+}) and this prevents the catalysts from being particularly active in oxidizing the organic material.^{11,12} This explains the high selectivity for benzonitrile formation on the V-P-O/ γ - Al_2O_3 catalysts.

The data in Table 1 show that ammonia uptake capacities of the catalysts correlate directly with toluene conversions. Thus, the ammoxidation of toluene takes place on the sites of the catalyst whose quantity is estimated by ammonia chemisorption. The acidity of the catalysts which NH_3 chemisorption estimates can be attributed to the presence of surface P-OH groups and to coordinatively unsaturated vanadium(IV) ions exposed in the surface coupled to V=O double bonds.¹³ This is in agreement with the report that ammonia chemisorption capacities correlate directly with *o*-xylene oxidation activity to give phthalic anhydride over V_2O_5 - TiO_2 (anatase) catalysts¹⁴ and with methanol oxidation activity over V_2O_5 supported on phosphate-modified alumina¹⁵ and phosphate-modified silica.¹⁶ The probable mechanism involves oxidized toluene being stabilized on the catalyst surface as benzoate ion, the adsorbed benzoate ion then reacting with ammonia to form benzonitrile. The reduced sites are then reoxidized by oxygen. Al_2O_3 is believed to stabilize the benzoate ion.¹⁷ Stable activity and selectivity for benzonitrile formation were observed for the whole period of study, 50 h. Thus, the V-P-O/ γ - Al_2O_3 catalysts have good potential to produce benzonitrile with about 98% selectivity via ammoxidation of toluene.

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